The Charges on Positive and Negative Ions in Gases.

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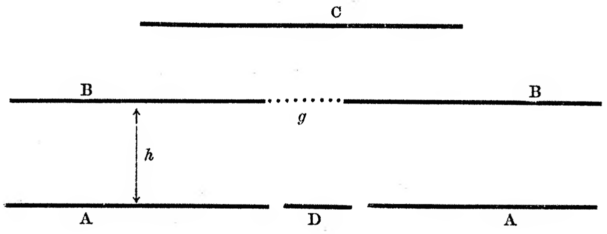
In a paper on the Diffusion of Ions in Gases,* I described a method of comparing the charges on the ions generated in gases with the charge on an ion in a liquid electrolyte. If N be the number of molecules in a cubic centimetre of a gas at standard pressure and temperature, and e the charge on an ion, then $N . e = 3{\cdot}10^{8} . U/K$, where U is the velocity of an ion in a field of unit electric force and K the coefficient of diffusion. Thus from separate determinations of the quantities U and K, the product $N . e$ can be obtained.

If E is the charge on a monovalent ion in a liquid electrolyte, $N . E = 1{\cdot}23 \times 10^{10}$, so that a comparison of the various charges may be made, and the calculations have shown that the charge on a positive or negative ion in a gas is nearly equal to the charge E. There were, however, considerable discrepancies, particularly with positive ions, which gave values of $N . e$ as great as $1{\cdot}66 \times 10^{10}$ in some cases.

Some time ago, while examining these investigations, I found that, by a somewhat different method, it would be possible to arrange an experiment for determining $N . e$ directly, and to arrive at much more accurate results than have been obtained hitherto.

In order to apply the principle, it is necessary to have the ions moving in a uniform field, and to find experimentally how they are distributed in some particular case. For this purpose two horizontal plates, A and B, were set at a distance h apart, and circular holes of the same radius were cut in the plates, the centres of the circles being in the same vertical line. A grating G of very fine wire was laid across the hole in the upper plate, and a metal disc D on an insulating support was fixed in the aperture of the lower plate, leaving a small air space between the disc and the plate, so that they should be insulated from each other.



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* John S. Townsend, 'Phil. Trans.,' A, 1899, vol. 193.

The plate B was maintained at a potential V, and a third plate C above B was maintained at a potential V′ greater than V and of the same sign. The lower plate and the disc were connected alternately to a sensitive electrometer, and during the course of an experiment their potentials did not differ appreciably from the zero.

The ions were generated in the air space between B and C by Röntgen rays, and positive or negative ions were driven to the grating according as the potential of C was positive or negative. The electric force being in the same direction above and below the grating, some of the ions pass through and travel under a constant electric force Z towards the central disc D. At the same time the ions diffuse laterally, so that some arrive on the disc and some on the plate. The greater the force Z the less time there will be for the diffusion, so the proportion of the total number that arrive at the disc increases with the force between A and B.

The ratio R of the number arriving at the disc to the total number was determined accurately with the aid of the electrometer.

The mathematical investigation of the distribution of the ions between the plates A and B can easily be made by considering the equations for the variation of the partial pressure p of the ions. The three equations corresponding to the three rectangular axes are of the form

$$\frac{1}{\mathrm{K}}(pu) = -\frac{dp}{dx} + n \,.\, \mathrm{X} \,.\, e,$$

where n is the number of ions per cubic centimetre (which is proportional to p), u the velocity and X the electric force along the axis of x.

Differentiating the three equations and substituting in the equation of continuity for the steady state,

$$\frac{d}{dx}(pu) + \frac{d}{dy}(pv) + \frac{d}{dz}(pw) = 0,$$

the following equation for p is obtained—

$$\frac{d^2p}{dx^2} + \frac{d^2p}{dy^2} + \frac{d^2p}{dz^2} = \mathrm{Z}e\frac{dn}{dz} = \frac{\mathrm{N} \,.\, e \,.\, \mathrm{Z}}{\mathrm{P}} \cdot \frac{dp}{dz},$$

where P is the pressure due to 760 mm. of mercury, at which pressure N is reckoned.

This latter equation shows that p at any point is a function of $(\mathrm{N} \,.\, e \,.\, \mathrm{Z})$. The constants in the solution $p = f(\mathrm{N} \,.\, e \,.\, \mathrm{Z})$ are functions of the position of the point and at the lower plate, where $z = h$, the ratio R may be obtained by integration. Thus $\mathrm{R} = \int_0^a rpdr \div \int_0^b rpdr$, where r is the distance from the centre of the disc, a and b being the radii of the disc D and the plate B respectively.

Hence $$\mathrm{R} = \phi\,(\mathrm{N}\,.\,e\,.\,\mathrm{Z}).$$

It is not necessary to know the form of the function ϕ in order to see how to compare the charge on a positive ion with that on a negative ion, or to compare the charges on ions in different gases.

Experiments made with positive and negative ions for the same intensity of force Z gave a value of R for positive ions which was much greater than the value for negative ions. This shows that the charge on a positive ion is greater than the charge on a negative ion. The same value of R, within 1 per cent., was obtained for the two kinds of ions when the force used with negative ions was double that used with positive ions. Letting $\underset{+}{e}$ denote the charge on a positive ion and $\underset{-}{e}$ the charge on a negative ion, then

$$\phi\,(\mathrm{N}\,.\,\underset{+}{e}\,.\,\mathrm{Z}) = \phi\,(\mathrm{N}\,.\,\underset{-}{e}\,.\,2\mathrm{Z})$$

for all values of Z.

Hence the charge on the positive ion is exactly double the charge on the negative ion. This shows that when a molecule of air is ionised by Röntgen rays, one positive ion and two negative ions are produced, the charge on the former being double that on either of the latter.

In order to find the absolute value of $\mathrm{N}\,.\,e$, it is necessary to solve the differential equation in p. An exact solution can easily be obtained which satisfies all the surface conditions, since p can be expanded in a series of Bessel's functions. The distribution being symmetrical round the axis of z joining the centre of the grating with the centre of the disc, the differential equation reduces to the form—

$$\frac{d^2p}{dr^2}+\frac{1}{r}\frac{dp}{dr}+\frac{d^2p}{dz^2} = \frac{\mathrm{N}\,.\,e\,.\,\mathrm{Z}}{\mathrm{P}}\frac{dp}{dz},$$

where r is the distance of a point from the axis.

Letting $$p = q\,.\,\epsilon^{-\theta^2 z},$$
the equation for q is

$$\frac{d^2q}{dr^2}+\frac{1}{r}\frac{dq}{dr} = \left(-\theta^2.\frac{\mathrm{N}\,.\,e\,.\,\mathrm{Z}}{\mathrm{P}}-\theta^4\right)q = -\lambda^2 q,$$

so that $$q = \mathrm{J}_0\,(\lambda r),$$

and $$p = \Sigma\mu \mathrm{J}_0\,(\lambda r)\,\epsilon^{-\theta^2 z}.$$

The values of μ and λ are determined from the surface conditions and θ^2 is the positive root of the equation

$$\theta^4+\theta^2\frac{\mathrm{N}\,.\,e\,.\,\mathrm{Z}}{\mathrm{P}} = \lambda^2.$$

Hence p can be found at any point of the lower plate, where $z = h$, and the integrations $\int_0^a prdr$ and $\int_0^b prdr$ can easily be obtained from the known properties of Bessel's functions. The connection between R and N . *e* . Z was thus found, and a curve was drawn to show the values of R for a series of values of N . *e* . Z. When R is found experimentally the corresponding value of N . *e* . Z can be found immediately from the curve. The expression for R in terms of N . *e* . Z is very complicated and I have to acknowledge my indebtedness to Mr. C. E. Haselfoot in having assisted in making the necessary calculations from the tables of Bessel's functions.

I have made a number of determinations of R with different forces, pressures, and intensities of ionisation, and they all agree in giving results in accurate accordance with the theory. The values found for N*e* are $2·41 \times 10^{10}$ for positive ions and $1·23 \times 10^{10}$ for negative ions. Each of these numbers represents the mean result of several different experiments in which none of the determinations differ from the mean value by more than 4 or 5 per cent., which shows that considerable accuracy can be obtained by this method.

When the value of N . *e* is deduced by the first method which I gave,* the numbers corresponding to the positive ions were about 10 or 20 per cent. higher than those for the negative ions. Thus, when the rates of diffusion are compared with the velocities given by Zeleny,† the values of $N . e \times 10^{-10}$ for positive ions in air, oxygen, and hydrogen are 1·46, 1·63, and 1·63, and the corresponding numbers for the negative ions were 1·31, 1·36, 1·25. These numbers taken alone would not justify the conclusion that the molecules are ionised in the way that I have just found, but a little consideration shows that the relative values are of the kind that should be expected. If the effect of recombination be considered, it will be seen that a positive ion would rapidly combine with a negative ion when the charge on the former is $2e$, as the force between them is $2e^2$. After combining with one negative ion, the force between the positive ion and another negative ion would be e^2, so that the second step towards complete recombination would not proceed so rapidly as the first. The result of this would be that after the positive and negative ions have been in the gas together for a short time, a large proportion of the positive ions would have one-half of their original charge.

The determinations of the coefficients of diffusion K were made with small ionisations that had been reduced by the process of recombination, and from a consideration of Zeleny's method of finding the velocities it is evident that recombination must have been going on in his experiments also. Under these circumstances the numbers obtained for N . *e* by the first method correspond to positive ions, of which some have a charge 2*e* and others a charge *e*. The discrepancies from the value $1 \cdot 23 \times 10^{10}$ obtained for the negative ions are not greater than what might have arisen from experimental errors.

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* J. S. Townsend, *loc. cit.*

† 'Phil. Trans.,' A, 1900, vol. 195.

In the experiments I have just now made the recombination must have been negligible, so that no appreciable number of the positive charges could have been reduced from 2*e* to *e*.

A full description of the experimental methods used in these determinations will be given in a future paper, when the experiments which are in progress with different gases are completed.